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<b>(21) International Application Number:</b> PCT/US96/10807 <b>(22) International Filing Date:</b> 24 June 1996 (24.06.96) <b>(30) Priority Data:</b> 499,355                      7 July 1995 (07.07.95)                      US <b>(71) Applicant:</b> OLIN MICROELECTRONIC CHEMICALS, INC. [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US).	<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
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<b>(54) Title:</b> REDOX REAGENT-CONTAINING POST-ETCH RESIDUE CLEANING COMPOSITION <b>(57) Abstract</b> A noncorrosive post-etch residue cleaning composition containing: (a) 1-70 % by weight of an organic polar solvent having a dipole moment of more than 3.5; (b) 1-70 % by weight of selected amine compounds having at least one hydroxyl group and a boiling point higher than 150 °C at atmospheric pressure; (c) 0.1-10 % by weight of selected amino acid having at least one hydroxyl group; (d) 1-20 % by weight of selected redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7); and (e) 0.90 % by weight of water.		

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REDOX REAGENT-CONTAINING POST-ETCH RESIDUE  
CLEANING COMPOSITION

BACKGROUND OF THE INVENTION

1. Field of the Invention

5       The present invention relates to a noncorrosive cleaning composition for metal oxide-type, post-etch residues which contain the combination of (1) selected solvents; (2) selected amines; (3) selected corrosion inhibitors; (4) selected redox reagents; 10 optionally (5) water.

2. Description of the Prior Art

15       The photoresist stripper art is replete with numerous references to stripper combinations containing both a polar solvent and an amine compound. The presence of an amine in photoresist 20 stripper compositions has been judged to be essential to effectively remove resist film cross-linked by baking, plasma etching, ion implantation, or other LSI device manufacturing processes. However, amine-type photoresist strippers sometimes 25 have a serious problem of corrosion, especially with aluminum substrates.

It is believed that this corrosion proceeds by the ionization of water by the amine in post- 30 stripping water rinses, as residual stripper solution may be retained on the substrate surface and/or substrate carrier after the stripping step. In other words, the amine component of the stripper composition does not corrode the substrate, but may trigger water to cause the corrosion.

To solve this problem, an intermediate rinse step with an organic solvent has been used between the stripping step and the post-stripping rinse with water. For example, isopropyl alcohol is known to  
5 be useful for this purpose. However, such intermediate rinses are not necessarily desirable because overall stripping operation becomes more complicated and, furthermore, an additional solvent waste is produced. Accordingly, if amine-type  
10 strippers are to be further employed, there is a need to solve this corrosion problem without intermediate organic solvent washes. The present invention provides such a solution.

During anisotropic plasma etching processes for  
15 via contacts, metal patterns, and passivation openings, "sidewall residues" are frequently deposited on the resist sidewall. After the oxygen plasma ashing of photoresist films, these residues become metal oxides. Incomplete removal of these  
20 residues interfere with the pattern definition and/or complete filling of via-holes.

Several different chemistries have been identified for removing the post-etch residues, in particular of the metal oxide type. For example,  
25 alkaline developers such as aqueous tetramethylammonium hydroxide (TMAH) are known to attack aluminum so that an aluminum oxide can be etched with TMAH. However, other types of the post-etch residues associated with multi-metal systems such as  
30 Al/Si/Cu cannot be so easily removed with TMAH. TMAH also is ineffective on residues from polysilicon plasma etch processes.

The metal oxide type sidewall residues can also be removed with: (1) a mixture of HF and ethylene glycol ether or (2) a mixture of nitric acid, acetic acid, and hydrofluoric acid. These solutions  
5 require extreme process control to prevent excessive attack of critical metal and oxide layers. In some device structures, these solutions are not useable because of their nonselective attack mechanisms.

Recently, Wai M. Lee described at The  
10 Interconnects, Contact Metallization and Multilevel Metallization Symposium (183rd Spring Meeting) of The Electrochemical Society, Inc. in Honolulu, Hawaii, May 16-21, 1993, that a hydroxylamine-  
15 containing stripper composition can remove some kinds of the sidewall residues.

Although hydroxylamine has a potential to remove the metal oxide type of the post-etch residues, it is not stable upon heating.

Accordingly, hydroxylamine is not suitable for  
20 the use of stripping of photoresist films or removing of the post-etch residues at higher temperatures.

Illustrative references suggesting photoresist stripper composition containing the combination of a  
25 polar solvent and an amine compound are the following:

1. U.S. Patent No. 4,617,251, which issued to Sizensky et al. on October 14, 1986, teaches a positive photoresist stripping composition  
30 containing (A) selected amine compound (e.g., 2-(2-aminoethoxy)-ethanol; 2-(2-aminoethylamino)-ethanol; and mixtures thereof) and (B) selected polar solvents (e.g., N-methyl-2-pyrrolidinone, tetra-

hydrofurfuryl alcohol, isophorone, dimethyl sulfoxide, dimethyl adipate, dimethyl glutarate, sulfolane, gamma-butyrolactone, N,N-dimethylcetamide and mixtures thereof). The reference  
5 further teaches that water as well as dyes or colorants, wetting agents, surfactants and antifoamers may be added into this composition.

2. U.S. Patent No. 4,770,713, which issued to Ward on September 13, 1988, teaches a positive  
10 photoresist stripping composition containing (A) a selected amide (e.g., N,N-dimethyl acetamide; N-methyl acetamide; N,N-diethyl acetamide; N,N-dipropyl acetamide; N,N-dimethyl propionamide; N,N-diethyl butyramide and N-methyl-N-ethyl propion-  
15 amide) and (B) selected amine compound (e.g., monoethanolamine, monopropanolamine, methylaminoethanol). The patent also teaches this stripper may optionally contain a water miscible nonionic detergent (e.g., alkylene oxide condensates, amides  
20 and semi-polar nonionics).

3. U.S. Patent No. 4,786,578, which issued to Neisius et al. on November 22, 1988, teaches a rinse solution used after a photoresist stripper, said  
25 rinse solution containing (A) a nonionic surfactant (e.g., ethoxylated alkylphenol, fatty and ethoxylate, fatty alcohol ethoxylate or ethylene oxide/propylene oxide condensate) and (B) an organic base (e.g., mono-, di-, or tri-ethanolamine).

4. U.S. Patent No. 4,824,762, which issued to  
30 Kobayashi et al. on April 25, 1989, teaches photoresist stripping post-rinse solution containing (A) glycol ether (e.g., diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether,

tripropylene glycol monomethyl ether) and (B) an aliphatic amine (e.g., monoethanolamine or triisopropylamine).

5 U.S. Patent No. 4,824,763, which issued to Lee on April 25, 1989, teaches positive-working photoresist stripping composition containing (A) triamine (e.g., diethylene-triamine) and (B) non-polar solvent (e.g., N-methyl-2-pyrrolidone, dimethylformamide, butyrolactone, aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons).

6. U.S. Patent No. 4,904,571, which issued to Miyashita et al. on February 27, 1990, teaches printed circuit board photoresist stripper composition containing (A) a solvent (e.g., water, alcohols, ethers, ketones, chlorinated hydrocarbons and aromatic hydrocarbons); (B) an alkaline compound dissolved in said solvent (e.g., primary amines, secondary amines, tertiary amines, cyclic amines, polyamines, quaternary ammonium amines, sulfonium hydroxides, alkali hydroxides, alkali carbonates, alkali phosphates and alkali pyrophosphates); and (C) a borohydride compound dissolved in said solvent (e.g., sodium borohydride, lithium borohydride, dimethyl amine borane, trimethyl amine borane, pyridane borane, tert-butyl amine borane, triethyl amine borane, and morpholine borane).

7. German Published Patent Application No. 3828513, which published on March 1, 1990 and is assigned to Merck patent GMBH, teaches a positive and negative photoresist stripper composition containing (A) an aprotic polar solvent (e.g., 1,3-dimethyl-2-imidazolidinone or 1,3-dimethyl-

tetrahydro-pyrimidinone); and (B) an organic base (e.g., alkanolamine).

8. Japanese Published Patent Application No. 56-115368, which was published on September 10, 1981 and is assigned to San Ei Chemical Industries, KK, teaches a photoresist stripping composition containing (A) nonionic surface activator (e.g., a polyethylene glycol ether); (B) organic solvent (e.g., cyclohexanone); and (C) either a swelling agent (e.g., polyethylene glycol) or penetrant (e.g., 2-aminoethanol).

9. Japanese Published Patent Application No. 63-208043, published on August 29, 1988, teaches a positive-working photoresist stripper composition containing (A) 1,3-dimethyl-2-imidazolidinone; (B) a water-soluble organic amine (e.g., monoethanolamine, 2-(2-aminoethoxy)-ethanol, triethylene(tetramine)). The application also teaches a surfactant may be added to the stripper.

10. Japanese Published Patent Application No. 1-081949, which published on March 28, 1989 and is assigned to Asahi Chemical, teaches a positive-working photoresist stripper composition containing (A) gamma-butyrolactone, N-methyl-formamide, N,N-dimethylformamide, N,N-dimethyl-acetoamide or N-methylpyrrolidone; (B) an amino alcohol (e.g., N-butyl-ethanolamine and N-ethyldiethanolamine); and (C) water.

11. Japanese Published Patent Application No. 4-350660, which is assigned to Texas Instruments, Japan and Kanto Chemical, Inc., teaches a stripper for positive photoresists comprising (A) 1,3-dimethyl-2-imidazolidinone (DMI), (B) dimethyl-



sulfoxide (DMSO) and (C) a water-soluble amine (e.g., monoethanolamine or 2-(2-aminoethoxy)ethanol wherein the amount of the water-soluble amine is 7-30% by weight.

5           12. U.S. Patent No. 5,279,791, which issued to Lee on January 18, 1994, teaches a stripping composition for removing resists from substrates containing (A) hydroxylamine (e.g.,  $\text{NH}_2\text{OH}$ ); (B) at least one alkanolamine; and optionally (C) at least  
10 one polar solvent.

          13. Japanese Published Patent Application No. 7-28254, which is assigned to Kanto Chemical, Inc., teaches a stripper for the sidewall residues comprising (a) a selected compound from sugar  
15 alcohols, isopropylalcohol, dimethylsulfoxide, and 1,3-dimethyl-2-imidazolidininone; (b) alkanolamine; (c) water; and optionally (d) quaternary ammonium hydroxides.

          None of these references suggest a complete  
20 solution for removing post-etch residues, particularly for the metal oxide type, without corrosion.

#### BRIEF SUMMARY OF THE INVENTION

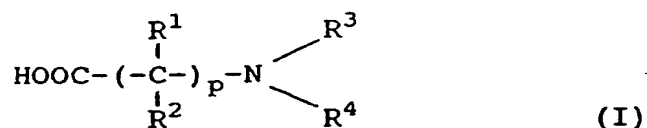
          The present invention, therefore, is directed to a post-etch residue cleaning composition  
25 comprising:

          (a) from about 1 to about 70% by weight of an organic polar solvent having a dipole moment of more than 3.5;

          (b) from about 1 to about 70% by weight of an  
30 amine compound having at least one hydroxyl group

per molecule and having a boiling point higher than 150°C at atmospheric pressure;

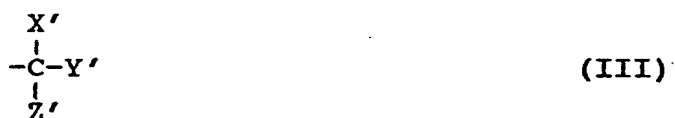
- (c) from about 0.1 to about 10% by weight of an amino acid selected from the group consisting of  
 5 compounds having the formula (I):



wherein p is an integer ranging from 1-3; R<sup>1</sup> and R<sup>2</sup> are each independently selected from the group consisting of hydrogen and compounds having the formula (II):



- 10 wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, alkyl, alkoxy, phenyl, and mono-, di- or tri-hydroxy-substituted phenyl groups; and R<sup>3</sup> and R<sup>4</sup> are each independently  
 15 selected from the group consisting of hydroxy and compounds having the formula (III):



wherein X', Y', and Z' are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OH, alkyl, or alkoxy group, and at least one of them is -OH, -CH<sub>2</sub>OH or -CH<sub>2</sub>CH<sub>2</sub>OH;

- 20 (d) from about 1 to about 20% by weight of a redox reagent having a redox potential in the range

between +1.0 V and -2.0 V vs. SHE (at pH=7) selected from the group consisting of sugar alcohols, isopropyl alcohol, catechol, piperidine, aniline, o-phenylenediamine, hydrazine, 1,10-phenanthroline and  
5 benzidine; and

(e) optionally, from about 0% to about 90% by weight of water; all percents based on the total weight of the cleaner composition.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 As stated above, the noncorrosive post-etch cleaner of the present invention has four critical components, namely:

(a) a polar solvent having a dipole moment of at least 3.5;

15 (b) an amine having at least one hydroxyl group per molecule and a boiling point higher than about 150°C at atmospheric pressure;

(c) an amino acid having at least one hydroxyl group;

20 (d) a redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7); and

(e) optionally, water.

The solvent used in this stripper composition  
25 should have a good solubility for other stripper components. The solvent is also necessary to efficiently remove cross-linked resist films which are strongly adhering to the substrate in combination with the amine.

30 The solvent should meet the following criteria:

(1) Its dipole moment should be more than 3.5.

(2) Its boiling point should preferably be more than 150-180°C.

(3) Its flash point should preferably be more than 80-90°C.

5        Among various candidates, amides and sulfoxides are particularly preferred. In particular, cyclic amides such as N-alkyl-2-pyrrolidones (e.g., N-hydroxyethyl-2-pyrrolidone) or 1,3-dialkyl-2-imidazolidinones as well as sulfoxides such as  
10        dimethylsulfoxide (DMSO) are especially preferable from a view point of stripping power and toxicity. A suitable solvent mixture may be an admixture of N-hydroxyethyl-pyrrolidone (HEP) with 1,3-dimethyl-2-imidazolidinone (DMI) or dimethylsulfoxide (DMSO)  
15        wherein the mixing ratio of HEP:DMI or DMSO is from about 95:5% to about 5:95% by weight as HEP is a known safer solvent and DMI is a powerful stripping solvent.

20        As mentioned above, another major component of the cleaner is an amine compound. Alkanolamines are particularly preferable. But some of them cannot efficiently dissolve cross-linked resist films by themselves, probably because of their high viscosity. In this case, those amines can be used  
25        with the above-mentioned polar solvents so that the resulting stripper solutions have a moderate viscosity.

30        Various amines can be used in the cleaner composition of this invention. Particularly, amines having at least one hydroxyl group, so-called alkanolamines, are the most preferable; for example, monoethanolamine, diethanolamine, triethanolamine;

2-(2-aminoethoxy)ethanol, 2-(2-aminoethyl-amino)ethanol, and the like.

The third critical component is a selected amino acid compound working as a corrosion  
5 inhibitor.

Examples of compounds within this class include: tricine, bicine, DL-homoserine, D-homoserine, L-homoserine, DL-threonine, D-allo-threonine, L-allo-threonine, D-threonine, L-  
10 threonine, DL-3-hydroxynorvaline, DL-methyltyrosine, D-4-hydroxyphenylglycine, DL-tyrosine, D-tyrosine, L-tyrosine, 3-(3,4-dihydroxyphenyl)-DL-alanine, 3-(3,4-dihydroxyphenyl)-L-alanine, 3-(2,4,5-trihydroxyphenyl)-DL-alanine, DL-alpha-  
15 methyltyrosine, L-alphamethyltyrosine, (-)-3-(3,4-dihydroxyphenyl)-2-methyl-L-alanine, DL-threo-3-phenylserine, DL-threo-3,4-dihydroxyphenylserine, and the like. Preferable candidates among them are tricine, bicine, 3-(3,4-dihydroxyphenyl)-DL-alanine,  
20 3-(2,4,5-trihydroxyphenyl)-DL-alanine, and DL-threo-3,4-dihydroxyphenylserine, in terms of cost/performance balance.

Examples of compounds outside the formula (I) which may be also useful for this function include:  
25 DL-4-amino-3-hydroxybutyric acid, (3's, 4's)-(-)-statine, (+)-muramic acid, 5-hydroxy-DL-lysine, cis-4-hydroxy-D-proline, cis-4-hydroxy-L-proline, trans-4-hydroxy-L-proline, mimosine, N-(4-hydroxyphenyl)glycine, 3,3',5-triiodo-L-thyronine, D-  
30 thyroxine, L-thyroxine, D-4-hydroxyphenylglycine, 3-nitro-L-tyrosine, 3-amino-L-tyrosine, 3,5-dinitro-L-tyrosine, chloroacetyl-L-tyrosine, N-acetyl-tryptosinamine, and the like.

It has been found that the presently claimed amino acid compounds of formula (I) can effectively inhibit corrosion without any damage of the stripping power of the claimed amines. For example, it is  
5 believed that amino acids having hydroxyl groups can form a complex with amines in stripper solutions to reduce basicity of stripper solution. This results in retardation of the corrosion.

In contrast, if an organic or inorganic acid is  
10 used instead of the compounds of formula (I), basicity of the amine-containing stripper solution is so much decreased that the stripper power can also be degraded as well. In other words, it is important to choose a moderate acidity of additives  
15 as a corrosion inhibitor. In particular, amino acids having hydroxyl group are desirable because the hydroxyl group attached can contribute to enhance a solubility of the resulting complex with amines.

20 The fourth critical component is a selected redox reagent working as a remover of the post-etch residues, particularly for the metal oxides. The metal oxides, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are not soluble in organic solvents at all and slightly soluble in  
25 water, particularly at high pH. The conventional stripper compositions do not dissolve these compounds.

To solubilize typical metal oxides formed by the typical plasma etching and oxygen plasma ashing  
30 processes, the redox reagents used in this invention should have a redox potential in the range from +1.0 V to -2.0 V vs. SHE at pH=7, more preferably in the range from +0.2 V to -1.0 V.

Examples of the redox reagents within this class include: (a) sugar alcohols such as erythritols, pentitols (e.g., D-arabitol and D-xylitol), hexitols (e.g., D-sorbitol and D-mannitol), and related reduced-type carbohydrates; (b) other types of alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and related derivatives; (c) phenolic compounds such as catechol, cresol, hydroquinone, trinitrophenol, and related derivatives; (d) amines like piperidine, ethylamine, aniline, o-phenylene diamine, hydrazine, and related compounds; (e) dyes such as methylene blue, pheno-safranine, neutral red, eriochrome, and related compounds; (f) other reducing reagents like acetic acid, oxalic acid, acetone, 1,10-phenanthroline, benzidine, and related compounds.

Optionally, water (preferably, deionized water) can be added to the cleaner composition of this invention, because some combinations of amines and amino acids tend to form a complex which is least soluble in organic solvents depending on a molar ratio of these two components. In that case, water is helpful to stabilize the stripper solution without precipitation. It should be noted that the presence of the amino acid will prevent corrosion occurring, even when water is present in the amine-containing cleaner composition.

The preferred amounts of these five ingredients are about 2-50% polar solvent; about 2-50% amine compound; about 0.5-8% amino acid corrosion inhibitor; about 3-10% redox reagent; and optionally about 0-50% water, all based on the weight of the cleaner composition.

Various other ingredients known to those skill in the art may optionally be included in the stripping composition, e.g., dyes or colorants, wetting agents, surfactants, antifoamers and so forth. Generally, the amount of each of these optional ingredients would be about 0.1-0.5% by weight, based on the total cleaner composition.

The described cleaner composition is used in removing post-etch residues, specially metal oxide type residues formed by oxygen plasma ashing of photoresist films after plasma etching of a metalized wafer. The method of the invention is carried out by contacting the metal oxide type residues with the described cleaner solution. The actual conditions, i.e., temperature, time, and the like, may vary over wide ranges and are generally dependent on the nature and thickness of the post-etch residues to be removed, as well as other factors familiar to those skilled in the art. In general, however, temperatures ranging from about 15°C to about 100°C for a period of about 5 minutes to about 60 minutes are typical.

A variety of means can be employed in contacting the post-etch residues with the cleaner solution in the practice of the invention. For example, the substrate containing the residues can be immersed in a cleaner bath or the cleaner solution can be sprayed over the surface of the post-etch residues, as will be apparent to those skilled in the art.

The present invention is further described in detail by means of the following Examples and Comparisons. All parts and percentages are by



weight and all temperatures are degrees Celsius unless explicitly stated otherwise.

#### EXAMPLE 1

5 A test wafer was prepared by CVD oxidation of the surface of silicon wafer, followed by sputtering Al-Cu-Si (Si 1 wt. %; Cu 0.5 wt. %) onto the silicon oxide layer. Thus prepared wafers were coated with a positive photoresist film, OiR 32 produced at OCG, at a film thickness of 1.0  $\mu$ m, baked, exposed  
10 imagewise, and developed under ordinary conditions. Then, the patterned wafers were baked at 150°C for 30 minutes and etched with a chlorine gas-based plasma, followed by oxygen plasma ashing of the photoresist film.

15 Thus obtained wafers, on which metal oxide type of the post-etch residues were remaining, were immersed in a bath of the cleaning solution which is consisting of N-methyl-2-pyrrolidone (5 wt. %), diethyleneglycolamine (5 wt. %), tricine (3 wt. %),  
20 D-sorbitol (5 wt. %), and deionized water (82 wt. %) at 25°C for 60 seconds, followed by water rinse for 3 minutes.

The wafer surface was observed under microscope to see the residues remaining. The surface  
25 resistivity was also determined to measure the corrosion of the metal substrate. The post-etch residues were completely removed and no corrosion was detected.

EXAMPLE 2

The preparation of the test wafer and the method of the test were the same as described in Example 1. The cleaning composition in this example  
5 was consisting of N-methyl-2-pyrrolidone (35 wt. %), diethyleneglycolamine (35 wt. %), bicine (5 wt. %), D-arabitol (5 wt. %), and deionized water (20 wt. %).

There were no remaining post-etch residues and  
10 no corrosion was observed on the wafer surface.

REFERENCE 1

All the test procedures were the same as in Example 1, except for the cleaning composition. In this example, the test sample consisted of N-methyl-  
15 2-pyrrolidone (5 wt. %), diethyleneglycolamine (5 wt. %), D-sorbitol (5 wt. %), and deionized water (85 wt. %).

The post-etch residues were completely removed but the metal surface of the substrate was  
20 significantly corroded compared with the above examples.

REFERENCE 2

All the test procedures were the same as in Example 1, except for the cleaning composition. In this example, the test sample consisted of N-methyl-  
25 2-pyrrolidone (35 wt. %), diethyleneglycolamine (35 wt. %), bicine (5 wt. %), and deionized water (25 wt. %).

The post-etch residues were not removed like Examples 1 and 2, and the metal surface of the substrate was not corroded like Reference 1.

While the invention has been described above  
5 with reference to specific embodiments thereof, it  
is apparent that many changes, modifications, and  
variations can be made without departing from the  
inventive concept disclosed herein. Accordingly, it  
is intended to embrace all such changes, modifica-  
10 tions, and variations that fall within the spirit  
and broad scope of the appended claims.

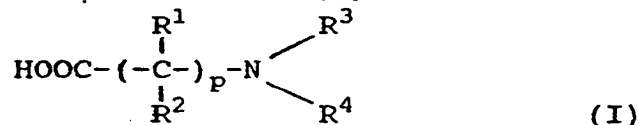
WHAT IS CLAIMED IS:

1. A post-etch residue cleaner composition, comprising:

5 (a) from about 1 to about 70% by weight of an organic polar solvent having a dipole moment of more than 3.5;

(b) from about 1 to about 70% by weight of an amine compound having at least one hydroxyl group per molecule and having a boiling point higher than  
10 150°C at atmospheric pressure;

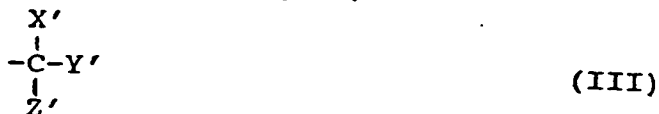
(c) from about 0.1 to about 10% by weight of an amino acid selected from the group consisting of compounds having the formula (I):



wherein p is an integer ranging from 1-3; R<sup>1</sup> and R<sup>2</sup>  
15 are each independently selected from the group consisting of hydrogen and compounds having the formula (II):



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, alkyl, alkoxy,  
20 phenyl, and mono-, di- or tri-hydroxy-substituted phenyl groups; and R<sup>3</sup> and R<sup>4</sup> are each independently selected from the group consisting of hydroxy and compounds having the formula (III):



wherein X', Y', and Z' are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OH, alkyl, or alkoxy group, and at least one of them is -OH, -CH<sub>2</sub>OH or -CH<sub>2</sub>CH<sub>2</sub>OH;

- 5 (d) from about 1 to about 20% by weight of a redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7) selected from the group consisting of sugar alcohols, isopropyl alcohol, catechol, piperidine, aniline, o-phenylenediamine, hydrazine, 1,10-phenanthroline and  
10 benzidine; and

(e) optionally, from about 0% to about 90% by weight of water; all percents based on the total weight of the cleaner composition.

- 15 2. The cleaner composition of claim 1, wherein said solvent (a) comprises a cyclic amide.

3. The cleaner composition of claim 2, wherein said cyclic amide is selected from the group consisting of N-alkyl-2-pyrrolidones and 1,3-dialkyl-2-imidazolidinones.  
20

4. The cleaner composition of claim 2, wherein said solvent (a) is an admixture of N-hydroxyethylpyrrolididone (HEP) with 1,3-dimethyl-2-imidozololidinone (DMI) wherein the ratio of HEP:DMI  
25 is from about 95:5% to about 5:95% by weight.

5. The cleaner composition of claim 1, wherein said solvent (a) comprises dimethylsulfoxide.

6. The cleaner composition of claim 1, wherein said solvent (a) is an admixture of N-hydroxyethylpyrrolididone (HEP) with dimethylsulfoxide (DMSO) wherein the ratio of HEP:DMSO is from 95:5% to about  
5 5:95% by weight.

7. The cleaner composition of claim 1, wherein said amine compound (b) is an alkanolamine.

8. The cleaner composition of claim 7, wherein said alkanolamine is selected from the group  
10 consisting of monoethanolamine, diethanolamine, triethanolamine, 2-(2-aminoethoxy)ethanol and 2-(2-aminoethylamino)ethanol.

9. The cleaner composition of claim 1, wherein said redox reagent (d) is a sugar alcohol.

15 10. The cleaner composition of claim 9, wherein said sugar alcohol is selected from the group consisting of erythritols, penitols, and hexitols.

11. The cleaner composition of claim 10, wherein said sugar alcohol is a penitol and is  
20 selected from the group consisting of D-arabitol and D-xylitol.

12. The cleaner composition of claim 10, wherein said sugar alcohol is a hexitol and is  
25 selected from the group consisting of D-sorbitol and D-mannitol.

13. The cleaner composition of claim 1, wherein said redox reagent (d) is isopropyl alcohol.

14. The cleaner composition of claim 1, wherein said redox reagent (d) is catechol.

5 15. The cleaner composition of claim 1, wherein said redox reagent (d) is piperidine.

16. The cleaner composition of claim 1, wherein said redox reagent (d) is aniline.

10 17. The cleaner composition of claim 1, wherein said redox reagent (d) is o-phenylenediamine.

18. The cleaner composition of claim 1, wherein said redox reagent (d) is hydrazine.

15 19. The cleaner composition of claim 1, wherein said redox reagent (d) is 1,10-phenanthroline.

20. The cleaner composition of claim 1, wherein said redox reagent (d) is benzidine.

20 21. The cleaner composition of claim 1, wherein said redox reagent (d) is present from about 3% to about 10% by weight, based on the total weight of said cleaner composition.

22. The cleaner composition of claim 1, wherein said amino acid (c) is selected from the group consisting of tricine, bicine, DL-homoserine, D-homoserine, L-homoserine, DL-threonine, D-allo-  
5 threonine, L-allo-threonine, D-threonine, L-threonine, DL-3-hydroxy-norvaline, DL-methyltyrosine, D-4-hydroxyphenylglycine, DL-tyrosine, D-tyrosine, L-tyrosine, 3-(3,4-  
10 dihydroxyphenyl)-DL-alanine, 3-(3,4-dihydroxyphenyl)-L-alanine, 3-(2,4,5-trihydroxyphenyl)-DL-alanine, DL-alpha-methyltyrosine, L-alpha-methyltyrosine, (-)-3-(3,4-dihydroxyphenyl)-2-methyl-L-alanine, DL-threo-3-phenylserine, and DL-threo-3,4-  
15 dihydroxyphenylserine.

23. The cleaner composition of claim 21, wherein said amino acid is selected from the group consisting of tricine, bicine, 3-(3,4-  
dihydroxyphenyl)-DL-alanine, 3-(2,4,5-  
20 trihydroxyphenyl)-DL-alanine, and DL-threo-3,4-dihydroxyphenylserine.

24. The cleaner composition of claim 1, wherein said cleaner composition comprises from about 0% to about 90% by weight of water.



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/10807

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 7/32, 7/34

US CL : 510/176, 175, 488, 500, 493

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/176, 175, 488, 500, 493

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: amino acid, etching, pyrrolidone, dimethylsulfoxide

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US, 5,472,830 A (Honda) 05 December 1995, see abstract	1-24
Y, P	US, 5,507,978 A (Honda) 16 April 1996, see abstract.	1-24
Y	US, 4,617,251 A (Sizensky) 14 October 1986, see col. 2 lines 18-31, col. 3 lines 30-50.	1-24
Y	US, A, 4,306,933 (Da Fonte, Jr.) 22 December 1981, see col. 2 lines 57-66 and col. 3 lines 21-37.	1-24
Y	US, 4,720,332 B1 Coffey) 28 August 1990, see abstract, col. 5 lines 8-25.	1-12, 21-24
Y	US, 5,419,779 A (Ward) 30 May 1995, see abstract, col. 2 lines 50-61.	1-8, 14, 21-24

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

05 AUGUST 1996

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**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US96/10807**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 4,309,300 A (Danforth et al.) 05 January 1982, see abstract, col. 3 lines 23-30.	1-8, 13, 21-24
Y	US, 4,592,787 A (Johnson) 03 June 1986, see abstract, col. 3 line 63 to col. 4 line 2.	1-8, 13, 21-24

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C11D 7/32, 7/34</b>	<b>A1</b>	(11) International Publication Number: <b>WO 97/03175</b> (43) International Publication Date: 30 January 1997 (30.01.97)
(21) International Application Number: <b>PCT/US96/10807</b> (22) International Filing Date: 24 June 1996 (24.06.96) (30) Priority Data: 499,355 7 July 1995 (07.07.95) US (71) Applicant: <b>OLIN MICROELECTRONIC CHEMICALS, INC.</b> [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(72) Inventors: <b>HONDA, Kenji</b> ; 8 Plymouth Drive, Barrington, RI 02924 (US). <b>HURDITCH, Rodney</b> ; 63-65 Elmgrove Avenue, Providence, RI 02906 (US). (74) Agents: <b>SIMONS, William, A. et al.</b> ; Wiggin & Dana, One Century Tower, New Haven, CT 06508-1832 (US).		<b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>  Date of publication of the amended claims and statement: 13 February 1997 (13.02.97)
(54) Title: <b>REDOX REAGENT-CONTAINING POST-ETCH RESIDUE CLEANING COMPOSITION</b>		
(57) Abstract  A noncorrosive post-etch residue cleaning composition containing: (a) 1-70 % by weight of an organic polar solvent having a dipole moment of more than 3.5; (b) 1-70 % by weight of selected amine compounds having at least one hydroxyl group and a boiling point higher than 150 °C at atmospheric pressure; (c) 0.1-10 % by weight of selected amino acid having at least one hydroxyl group; (d) 1-20 % by weight of selected redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7); and (e) 0.90 % by weight of water.		

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## AMENDED CLAIMS

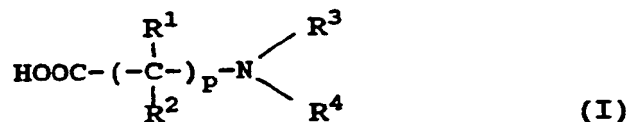
[received by the International Bureau on 17 January 1997 (17.01.97);  
original claims 1 and 8 amended; original claims 7, 13, 14 and 24 cancelled;  
new claim 25 added; remaining claims unchanged (5 pages)]

1. A post-etch residue cleaner composition comprising:

(a) from about 1 to about 70% by weight of an organic polar solvent having a dipole moment of more than 3.5;

(b) from about 1 to about 70% by weight of an alkanolamine compound having a boiling point higher than 150°C at atmospheric pressure;

(c) from about 0.1 to about 10% by weight of an amino acid selected from the group consisting of compounds having the formula (I):



wherein n is an integer ranging from 1-3; R<sup>1</sup> and R<sup>2</sup> are each independently selected from the group consisting of hydrogen and compounds having the formula (II):



wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, alkyl, alkoxy, phenyl, and mono-, di- or tri-hydroxy-substituted phenyl groups; and R<sup>3</sup> and R<sup>4</sup> are each independently selected from the group consisting of hydroxy and compounds having the formula (III):

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- 5 wherein X', Y', and Z' are each independently selected from hydrogen, -OH, -CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OH, alkyl, or alkoxy group, and at least one of them is -OH, -CH<sub>2</sub>OH or -CH<sub>2</sub>CH<sub>2</sub>OH;
- 10 (d) from about 1 to about 20% by weight of a redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7) selected from the group consisting of sugar alcohols, piperidine, aniline, o-phenylenediamine, hydrazine, 1,10-phenanthroline and benzidine; and
- 15 (e) optionally, from 0% to about 90% by weight of water; all percents based on the total weight of the cleaner composition.

2. The cleaner composition of claim 1 wherein said solvent (a) comprises a cyclic amide.

- 20 3. The cleaner composition of claim 2, wherein said cyclic amide is selected from the group consisting of N-alkyl-2-pyrrolidones and 1,3-dialkyl-2-imidazolidinones.

- 25 4. The cleaner composition of claim 2, wherein said solvent (a) is an admixture of N-hydroxyethylpyrrolididone (HEP) with 1,3-dimethyl-2-imidazolidinone (DMI) wherein the ratio of HEP:DMI is from about 95:5% to about 5:95% by weight.

- 30 5. The cleaner composition of claim 1, wherein said solvent (a) comprises dimethylsulfoxide.

6. The cleaner composition of claim 1, wherein said solvent (a) is an admixture of N-hydroxyethylpyrrolidone (HEP) with dimethylsulfoxide (DMSO) wherein the ratio of HEP:DMSO is from about 95:5% to about 5:95% by weight.

8. The cleaner composition of claim 1, wherein said alkanolamine is selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, 2-(2-aminoethoxy)ethanol and 2-(2-aminoethylamino) ethanol.

9. The cleaner composition of claim 1, wherein said redox reagent (d) is a sugar alcohol.

10. The cleaner composition of claim 9, wherein said sugar alcohol is selected from the group consisting of erythritols, penitols, and hexitols.

11. The cleaner composition of claim 10, wherein said sugar alcohol is a penitol and is selected from the group consisting of D-arabitol and D-xylitol.

12. The cleaner composition of claim 10, wherein said sugar alcohol is a hexitol and is selected from the group consisting of D-sorbitol and D-mannitol.

15. The cleaner composition of claim 1, wherein said redox reagent (d) is piperidine.

16. The cleaner composition of claim 1, wherein said redox reagent (d) is aniline.

17. The cleaner composition of claim 1, wherein said redox reagent (d) is o-phenylenediamine.

18. The cleaner composition of claim 1, wherein said redox reagent (d) is hydrazine.

5 19. The cleaner composition of claim 1, wherein said redox reagent (d) is 1,10-phenanthroline.

20. The cleaner composition of claim 1, wherein said redox reagent (d) is benzidine.

10 21. The cleaner composition of claim 1, wherein said redox reagent (d) is present from about 3% to about 10% by weight, based on the total weight of said cleaner composition.

15 22. The cleaner composition of claim 1, wherein said amino acid (c) is selected from the group consisting of tricine, bicine, DL-homoserine, D-homoserine, L-homoserine, DL-threonine, D-allo-threonine, L-allo-threonine, D-threonine, L-threonine, DL-3-hydroxy-norvaline, DL-methyltyrosine, D-4-hydroxyphenylglycine, DL-tyrosine, D-tyrosine, L-tyrosine, 3-(3,4-dihydroxyphenyl)-DL-alanine, 3-(3,4-dihydroxyphenyl)-L-alanine, 3-(2,4,5-trihydroxyphenyl)-DL-alanine, DL-alpha-methyltyrosine, L-alpha-methyltyrosine, (-)-3-(3,4-phenylserine, and DL-threo-3,4-25 dihydroxyphenylserine.

23. The cleaner composition of claim 21, wherein said amino acid is selected from the group consisting of tricine, bicine, 3-(3,4-dihydroxyphenyl)-DL-alanine, 3-(2,4,5



trihydroxyphenyl)-DL-alanine, and DL-threo-3,4-dihydroxyphenylserine.

25. The cleaner composition of claim 1, wherein said cleaner composition further comprises water.

## STATEMENT UNDER ARTICLE 19

Applicant's invention, as embodied in Claim 1, is drawn to a post-etch residue cleaner composition, comprising, among other things, from about 1 to about 70% by weight of an alkanolamine compound having a boiling point higher than 150°C at atmospheric pressure; and from about 1 to about 20% by weight of a redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE (at pH=7) selected from the group consisting of sugar alcohols, piperidine, aniline, o-phenylenediamine, hydrazine, 1,10-phenanthroline and benzidine.

Applicant submits that none of the references cited in the International Search Report teach or suggest a stripper composition that includes a redox reagent having a redox potential in the range between +1.0 V and -2.0 V vs. SHE selected from the group consisting of sugar alcohols, piperidine, aniline, o-phenylenediamine, hydrazine, 1,10-phenanthroline and benzidine.